

V. Buturlim, PhD. Thesis, opinion of supervisor

The PhD thesis of Volodymyr Buturlim, “**U in metastable systems: structure, magnetism, superconductivity**”, represents part of research results of the candidate obtained in the period 2015-2020. A complete account of his research effort would be rather extended. Numerous results and activities remained beyond the borderline, imposed so as to have the thesis thematically focused, with its size not exceeding a usual practice.

A common denominator of the work presented were metastable U-based alloys. Such alloys are of a significant technological importance, as transition metal atoms dissolved in the U matrix impede the phase transformation into a brittle orthorhombic structure. The high temperature *bcc* phase, stabilized or retained to low temperatures, is therefore a convenient nuclear fuel with high density of uranium. In this direction Vova Buturlim followed his predecessor Ilya Tkach, who started an intensive research of electronic properties of U-Mo alloys, which allowed to extrapolate and estimate features of pure *bcc* uranium at low temperatures. By means of a rapid solidification technique called splat cooling, the candidate followed the research focusing on Ti and Nb as alloying elements. Besides the phase stability, the main outcome of the work is description of superconductivity, which, as a rule, has very high upper critical fields. While the Mo case, Ti and Nb with U provides at high temperatures a contiguous area of the *bcc* phase throughout the whole binary phase diagram. A complete concentration range was covered for Ti. This allowed to address, still within the same phase, even the Ti-rich area. Interesting superconducting temperature and especially critical field enhancement was observed around 20% U. The field of 16 T for a BCS superconductor with T_C below 4 K is truly unique. Moreover, it was found that U does not develop a local moment when diluted in Ti matrix, indicating a strong *5f-3d* hybridization, expected for two electropositive metals.

The other part of the work was dealing with related hydrides. Besides crystal structure determination, indicating in most of cases the well known β -UH₃ structure with variable grain size, the main interest was in the variations of the ferromagnetic Curie temperature. The fact that similar variations of T_C , increasing generally with alloying of any transition metal attempted, led eventually to the recognition that the role of T metals occupying the U positions is mainly to vary the U/H ratio, which directly tunes the ferromagnetism. Hence the alloying of Ti, which forms relatively strong bonds with H, has a smaller impact than more inert Nb and eventually Mo, the last one leaving effectively all H-1s electrons to interact with relevant U states (mainly *6d* and *7s*).

Covering the extended U-Ti range allowed the candidate to address one old problem, the existence of UTi₂H_x Laves phases, reported 25 years ago in the context of a hydrogen storage project in Japan, but without any details related to properties of such substances. The puzzling fact in this context was that there is no Laves phase UTi₂ without hydrogen. The study, which was never repeated with a similar outcome, was therefore seriously doubted. V. Buturlim undertook a series of technological experiments. It soon turned out that only a very specific procedure (as to temperatures and H gas pressures) allows to avoid formation of more stable binary hydrides of U and Ti. This study amounted in synthesis of two Laves phases, namely UTi₂H₅ and UTi₂H₆, with different lattice parameters. A fortuitous fact was that the former one could be produced as monolithic material, allowing a full suite of experimental techniques to be employed for characterization. Extended transport studies including less common techniques as thermal conductivity and thermopower together with heat capacity identified UTi₂H₅ as a heavy fermion material with a significant disorder (due to incomplete occupation of H sites), giving a linear resistivity at low temperatures, predicted in some theoretical models. UTi₂H₆ is then a regular ferromagnet, far from the onset of magnetism.

In all the U hydride studies point to the significant U-H bonds, going beyond the normal concept of taking H primarily as stimulus for lattice expansion. Thus the reason for the formation of Laves phases, formed normally between two metals of different size, can be extended if we consider the U-H unit as metal A and Ti as metal B. Indeed we get then the A/B ration close to the ideal value 1.225.

The thesis illustrates that Vova Buturim succeeded to handle numerous and very diverse experimental techniques, involving technologies, characterization by diffraction or SEM, as well as cryogenic techniques. Driven by his curiosity, he was never tired of changing conditions of synthesis or modifying experimental facilities, writing new software, or repairing systems which just malfunctioned. A specific feature, not commonly encountered these days, is his tendency to study original articles, sometimes historical ones 50 or more years old. The thesis has been written reflecting his specific style. Avoiding copying extended paragraphs from existing literature, quite common this time in the theoretical part, he narrated quite well chosen blocks in his own way. In few isolated cases it led to certain problem of understanding, but in general the thesis is a well written fresh text, explaining even complicated issues by a simple language with a personal touch. The text contains a very limited number of omissions or mistakes.

As summary, I am convinced that the thesis, which proves a broad scope and capabilities of independent research of the candidate, is a solid basis for the PhD degree. In a broader context it demonstrates a potential of advanced diagnostic tools as high-resolution EBSD in solving complex issues of superconducting and magnetic materials.

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